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CLAIMS

[Claim(s)]

[Claim 1]A negative electrode which has for Li the negative electrode active material in which a dope and a dedope are possible reversibly.

An anode which has for Li the positive active material in which a dope and a dedope are possible reversibly.

Nonaqueous electrolyte.

It is the nonaqueous electrolyte secondary battery provided with the above, and the above-mentioned negative electrode active material contains a metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy at least.

[Claim 2]The nonaqueous electrolyte secondary battery according to claim 1, wherein the above-mentioned metallic material contains nickel₃Sn₄ and/or nickel₃Sn₂.

[Claim 3]The nonaqueous electrolyte secondary battery according to claim 1, wherein true density of the above-mentioned metallic material is more than 6.5 g/cm³.

[Claim 4]The nonaqueous electrolyte secondary battery according to claim 1, wherein the above-mentioned metallic material contains a nickel₃Sn₄ phase whose size of microcrystal of the [311] directions is 20 nm or less.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a nonaqueous electrolyte secondary battery.

[0002]

[Description of the Prior Art]In recent years, portable electronic equipment appears mostly and the small weight saving is attained. In connection with this, the small weight saving is repeatedly called for also about the chargeable and dischargeable rechargeable battery as a portable power supply of these electronic equipment. For this reason, the research and development for raising the energy density of a rechargeable battery are furthered actively.

[0003]Since the nonaqueous electrolyte secondary batteries which used for the negative electrode the carbon material in which a dope and a dedope of lithium are possible as a highly efficient rechargeable battery, for example are a light weight and high capacity, they are put in practical use by portable electronic device uses, such as a cellular phone and a notebook sized personal computer, and have spread.

[0004]

[The technical problem which an invention considers as solution use] In order to realize the cell of high energy density, unit volume, or the dope and dedope capacity per weight is high, and development of an available negative pole material is also effectively furthered in lithium.

[0005]For example, the rechargeable battery which used for negative electrode active material the metallic material which alloying with lithium is publicly known as for metal or semimetals, such as aluminum, germanium, Si, Sn, Zn, and Pb, and alloys these is examined (JP,10-223221,A, JP,10-162823,A). The rechargeable battery which used iron silicide, nickel silicide, and manganese silicide for negative electrode active material is examined (JP,5-159780,A, JP,8-153517,A, JP,8-153538,A). However, since the nonaqueous electrolyte secondary battery using such negative electrode active material has the bad cycle characteristic, it has

not resulted in utilization.

[0006]In this invention, it is proposed in view of such the conventional actual condition, and a metallic material is used as negative electrode active material.

Therefore, it is very high capacity and aims at providing the nonaqueous electrolyte secondary battery which is high performance rather than before.

[0007]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a nonaqueous electrolyte secondary battery concerning this invention, In a nonaqueous electrolyte secondary battery which has a negative electrode which has for Li the negative electrode active material in which a dope and a dedope are possible reversibly, an anode which has for Li the positive active material in which a dope and a dedope are possible reversibly, and nonaqueous electrolyte, Negative electrode active material contains a metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy at least.

[0008]In a nonaqueous electrolyte secondary battery concerning this invention constituted as mentioned above, negative electrode active material contains a metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy at least. Thereby, unit volume, and dope and dedope capacity of a nonaqueous electrolyte secondary battery per unit weight are high, and it has an available negative electrode for lithium effectively.

[0009]

[Embodiment of the Invention]Hereafter, the concrete embodiment of this invention is described in detail, referring to drawings.

[0010]The nonaqueous electrolyte secondary battery which applied this invention is provided with an anode, a negative electrode, and an electrolyte as a fundamental component.

[0011]And in this invention, the thing containing the metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy at least is used as negative electrode active material. As for this metallic material, specifically, it is preferred to contain $\text{nickel}_3\text{Sn}_4$ and/or $\text{nickel}_3\text{Sn}_2$. In the metallic material, Sn and/or nickel may contain in single phase.

[0012]Conventionally, the negative electrode active material of this kind of nonaqueous electrolyte secondary battery contained the metallic material which consists of Li and an element to alloy. Since Li and the element to alloy were accompanied by the big volume change when alloying them with Li, there was a problem that the nonaqueous electrolyte secondary battery using this negative electrode active material had a bad cycle characteristic.

[0013]Then, negative electrode active material thought that the volume change as the whole

negative electrode active material was controlled by containing the metallic material which made Li, Sn and Li which are the elements to alloy, and nickel which is the elements which are hard to alloy live together. Since Li and Co which is the elements which are hard to alloy are metal, the work as a conducting agent is also expectable. This thought that this negative electrode active material could realize improvement in a load characteristic.

[0014]Therefore, the nonaqueous electrolyte secondary battery which uses this negative electrode active material has per unit volume, and high dope and dedope capacity per unit weight, and it has an available negative electrode for lithium effectively.

[0015]Thereby, the nonaqueous electrolyte secondary battery which uses this negative electrode active material has per unit volume, and high dope and dedope capacity per unit weight, and it has an available negative electrode for lithium effectively.

[0016]As for the true density of a metallic material, it is more preferred that it is a range below 8.5 g/cm^3 that it is more than 6.5 g/cm^3 in more than good **** and 6.5 g/cm^3 . As for the true density of a metallic material, it is preferred to ask in accordance with the measuring method specified, for example to JISR7212. When the true density of a metallic material is lower than 6.5 g/cm^3 , the negative electrode active material containing this metallic material has a possibility of becoming what cannot use lithium effectively. Therefore, when the true density of a metallic material is more than 6.5 g/cm^3 , as a nonaqueous electrolyte secondary battery, it has an available negative electrode for lithium more effectively.

[0017]As for a metallic material, it is preferred that the size of the microcrystal of the [311] directions contains the $\text{nickel}_3\text{Sn}_4$ phase which is 20 nm or less. This has a negative electrode with higher dope and dedope capacity of lithium as a nature rechargeable battery of water electrolysis.

[0018]It is also possible to use together a metallic material which was mentioned above, and the conventionally publicly known negative electrode active material usually used with this kind of nonaqueous electrolyte secondary battery. As negative electrode active material which can be used together, a dope and the thing which has possible dedoping, for example, a carbon material etc., are mentioned in lithium.

[0019]Although a nonaqueous electrolyte secondary battery is provided with the component of an anode, an electrolyte besides [which has the negative electrode active material mentioned above] a negative electrode, etc., other components can use the conventional thing and the same thing.

[0020]Hereafter, a button type cell is made into an example and the component of a nonaqueous electrolyte secondary battery is explained.

[0021]As shown in drawing 1, the button type nonaqueous electrolyte secondary battery 1 The negative electrode 2, In having the separator 6 allotted between the negative electrode can 3

which accommodates the negative electrode 2, the anode 4, the positive electrode can 5 which accommodates the anode 4, and the anode 4 and the negative electrode 2, and the insulating gasket 7 and using an electrolysis solution as an electrolyte, it comes to fill up nonaqueous electrolyte in the negative electrode can 3 and the positive electrode can 5. In using a solid electrolyte and a gel electrolyte as an electrolyte, it forms a solid electrolyte layer and a gel electrolyte layer on the active material layer of the negative electrode 2 or the anode 4.

[0022]It comes to form a negative electrode active material layer by the negative electrode's 2 applying the negative electrode mixture containing the negative electrode active material which a dope and a dedope are reversibly possible, and explained Li previously on the negative pole collector, and a binder, and drying. As a negative pole collector, copper foil, nickel foil, etc. are used, for example.

[0023]As a binder contained in a negative electrode active material layer, the publicly known resin material etc. which are usually used can be used as a binding material of the negative electrode active material layer of this kind of cell. It is possible to add the publicly known additive agent etc. which are usually used for this kind of cell in a negative electrode active material layer.

[0024]The negative electrode can 3 accommodates the negative electrode 2, and serves as an external negative electrode of the nonaqueous electrolyte secondary battery 1.

[0025]When the anode 4 applies the positive electrode mixture which contains reversibly the positive active material and the binder in which a dope and a dedope are possible and dries Li on a positive pole collector, it comes to form a positive active material layer. As a positive pole collector, aluminium foil etc. are used, for example.

[0026]As positive active material, a metallic oxide, metallic sulfide, or specific polymers can be used according to the kind of cell made into the purpose. For example, as positive active material, the metallic sulfide or the oxide which does not contain lithium, such as CoS_2 , MoS_2 , NbSe_2 , and V_2O_5 , can be used.

[0027]The lithium multiple oxide etc. which make a subject the compound expressed with general formula LiM_xO_2 (M expresses the transition metal more than a kind at least among a formula, and x changes with charge-and-discharge states of a cell, and is usually $0.05 \leq x \leq 1.10$.) can be used as positive active material. As the transition metal M which constitutes this lithium multiple oxide, Co, nickel, Mn, etc. are preferred. As an example of these lithium multiple oxides, LiCoO_2 , LiSnO_2 , $\text{Li}_x\text{nickel}_y\text{Co}_{1-y}\text{O}_2$ (x and y change with charge-and-discharge states of a cell among a formula, and it is usually $0 < x < 1$ and $0.7 < y < 1.02$), LiMnO_4 , etc. can be mentioned. These lithium multiple oxides can generate high tension, and serve as positive active material outstanding in energy density.

[0028]Such positive active material may be used for the anode 4 by an one-kind independent,

and two or more sorts may be mixed and used for it.

[0029]As a binder contained in a positive active material layer, the publicly known resin material etc. which are usually used can be used as a binding material of the positive active material layer of this kind of cell. The binding material is unnecessary when metal lithium foil is used as positive active material.

[0030]It is possible to add the publicly known conducting agent usually used for this kind of cell, an additive agent, etc. in a positive active material layer.

[0031]The positive electrode can 5 accommodates the anode 4, and serves as an external anode of the nonaqueous electrolyte secondary battery 1.

[0032]An electrolyte may be what is called a liquefied electrolysis solution, and may be a solid electrolyte and a gel electrolyte.

[0033]When using an electrolyte as an electrolysis solution, as a nonaqueous solvent, various nonaqueous solvents usually used for the nonaqueous electrolyte of this kind of cell can be used. Specifically Propylene carbonate, ethylene carbonate, dimethyl carbonate, Organic solvents, such as diethyl carbonate, dimethoxymethane, diethoxyethane, gamma-butyrolactone, a tetrahydrofuran, 2-methyltetrahydrofuran, sulfolane, and 1,3-dioxolane, are mentioned. One kind may be used alone, and these nonaqueous solvents can also mix and use two or more kinds.

[0034]In using an electrolyte as a solid electrolyte or a gel electrolyte, As a polymer material to be used, silicon gel, acrylic gel, acrylonitrile gel, As fluorine system polymer, such as polyphosphazene denaturation polymer, polyethylene oxide, polypropylene oxide and these compound polymer, crosslinked polymer, denaturation polymer, For example, poly (vinylidene fluoro RAIDO) and poly (vinylidene fluoro Reid co-hexafluoropropylene), Although poly (vinylidene fluoro Reid co-tetrafluoroethylene), poly (vinylidene fluoro Reid co-trifluoroethylene), etc. can carry out various use of these mixtures, of course, it is not limited to these.

[0035]The salt of light metals, such as lithium, sodium, and aluminum, can be used for the light metal salt in which the above-mentioned electrolyte is dissolved (compatibility), and it can provide in it suitably according to the kind of cell.

[0036]For example, when it constitutes a rechargeable lithium-ion battery, specifically, Lithium salt, such as LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , LiAsF_6 , LiCl , LiBr , $\text{LiB}(\text{C}_6\text{H}_5)_4$, and $\text{LiSn}(\text{SO}_2\text{CF}_3)_2$, can be used.

[0037]The separator 6 can make the anode 4 and the negative electrode 2 able to estrange, and a publicly known material usually used can be used for it as a separator of this kind of nonaqueous electrolyte secondary battery. For example, the high polymer film etc. which consist of a nonwoven fabric and porous materials (specifically polypropylene etc.) provided with liquid permeability are used. When a solid electrolyte and a gel electrolyte are used as an

electrolyte, it is not necessary to necessarily form this separator 6.

[0038]The insulating gasket 7 is incorporated and united with the negative electrode can 3. This insulating gasket 7 is for preventing a break through of the nonaqueous electrolyte with which it filled up in the negative electrode can 3 and the positive electrode can 5.

[0039]In the nonaqueous electrolyte secondary battery 1 constituted as mentioned above, negative electrode active material contains the metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy at least. Specifically, $\text{nickel}_3\text{Sn}_4$ and/or $\text{nickel}_3\text{Sn}_2$ are contained. Therefore, as this nonaqueous electrolyte secondary battery 1, it has very high capacity, and has the high performance which is not in the former.

[0040]The true density of a metallic material has higher capacity as the nonaqueous electrolyte secondary battery 1 by being more than 6.5 g/cm^3 .

[0041]The metallic material which makes it come to alloy nickel and Sn has higher capacity as the nonaqueous electrolyte secondary battery 1 by containing the $\text{nickel}_3\text{Sn}_4$ phase whose size of the microcrystal of the [311] directions is 20 nm or less.

[0042]The nonaqueous electrolyte secondary battery concerning this invention is not limited in particular for shape, and can make cylindrical, a square shape, a button type, etc. a thin shape, large-sized **, and arbitrary sizes.

[0043]

[Example]Hereafter, the nonaqueous electrolyte secondary battery which applied this invention is explained based on a concrete experimental result.

[0044]Here, two or more nonaqueous electrolyte secondary batteries using two or more negative electrode active material and these negative electrode active material were first produced as a sample. And the battery characteristic was evaluated to the difference of negative electrode active material using these samples.

[0045]The manufacturing method of sample 1 negative electrode is as follows. First, the metallic material used as negative electrode active material was produced. Weighing of the Sn powder which is the Ni powder and Li which are introduction, and Li and the element which is hard to alloy, and an element to alloy was carried out, and it was used as powder mixture so that it might be set to 1:1 by an atomic ratio. Next, this powder mixture 5g was put into the pot for ball mills, and it sealed in argon atmosphere, and alloyed by performing ball mill operation for 27 hours using 25 steel balls 10 mm in diameter. And the alloyed powder mixture was classified and a metallic material of 75 micrometers or less was obtained.

[0046]Next, polyvinylidene fluoride was mixed with 75 weight sections for graphite powder as a conducting agent, five weight sections were mixed with 20 weight sections for the metallic material produced as mentioned above as negative electrode active material as a binder, and

negative electrode mixture was produced. Next, this negative electrode mixture was distributed in the N-methyl-2-pyrrolidone which is a solvent, and it was considered as the negative electrode mixture slurry. And applied, the SUS mesh state used as a negative pole collector was made to dry this negative electrode mixture slurry uniformly, and the negative electrode active material layer was formed.

[0047]And it was considered as the negative electrode by a diameter's being 15.5 mm and piercing the SUS mesh in which the negative electrode active material layer was formed to disc-like. A 50-mg active material is supported by this one negative electrode.

[0048]As an anode, thickness used what pierced the lithium metal foil which is 1.85 mm to a negative electrode and approximately isomorphism. As an electrolysis solution, nonaqueous electrolyte was prepared by dissolving LiPF_6 in the amount mixed solvent of isochore of propylene carbonate and dimethyl carbonate by the concentration of 1 mol/l.

[0049]The anode produced by making it above was accommodated in the positive electrode can, the negative electrode was accommodated in the negative electrode can, and the separator was allotted between the anode and the negative electrode. Nonaqueous electrolyte was poured in into the positive electrode can and the negative electrode can, and the button type test cell was produced by fixing a positive electrode can and a negative electrode can in total. The micropore film made from polypropylene was used as a separator.

[0050]Sample 2Li was used in the element which is hard to alloy, and the test cell was produced like the sample 1 except using the metallic material which alloyed the powder mixture which carried out weighing of the end of Fe powder, and Sn powder so that it might be set to 1:1 by an atomic ratio as negative electrode active material using Fe.

[0051]The test cell was produced like the sample 1 except having mixed [graphite powder] five weight sections with 95 weight sections for polyvinylidene fluoride as a binder, and having produced negative electrode mixture, using graphite powder as sample 3 negative electrode active material.

[0052]True density was measured about the negative electrode active material of the sample 1 produced as mentioned above - the sample 3. This measuring method is shown below.

[0053]<True density> The true density (ρ_B) of the negative electrode active material of these was measured in accordance with the measuring method provided in JISR7212, and it asked for it by calculating using the formula shown in several 1.

[0054]

[Equation 1]

$$\rho_B = \frac{(m_2 - m_1)(m_3 - m_1)d}{\left\{ (m_2 - m_1) - (m_4 - m_3) \right\} (m_5 - m_1)}$$

[0055]Here, d is the specific gravity (0.9946) at 30 °C of water. The value obtained by the method shown below was used for m_1 in the formula 1 - m_5 .

[0056]First, the mass (m_1) of the specific gravity bottle with a by-pass which is the content volume of about 40 ml is measured correctly. Next, negative electrode active material is put into a specific gravity bottle, and it is made for thickness to be set to about 10 mm from the bottom of a specific gravity bottle. And the mass (m_2) of the specific gravity bottle into which negative electrode active material was put is measured correctly.

[0057]Next, 1-butanol is calmly added to the specific gravity bottle into which negative electrode active material was put, and it is made for the depth to be set to about 20 mm from the bottom of a specific gravity bottle.

[0058]Next, a light vibration is added to this specific gravity bottle, and after checking that generating of big air bubbles has been lost, it puts in a vacuum desiccator, it exhausts gradually, and is made for a pressure to serve as 2.0 - 2.7kPa. When this pressure is maintained for more than 20 minutes and generating of air bubbles stops, a specific gravity bottle is taken out from a vacuum desiccator.

[0059]Next, 1-butanol is filled to a specific gravity bottle, and a plug is carried out, it dips in a high-temperature-hot-water tub 15 minutes or more, and the oil level of 1-butanol is doubled with the marked line. What is adjusted to 30 °C ± 0.03 °C is used for a high-temperature-hot-water tub. And after taking out this specific gravity bottle from a high-temperature-hot-water tub, cooling and considering it as a room temperature and isothermal, mass (m_3) is measured correctly.

[0060]Next, the specific gravity bottle filled only with 1-butanol is dipped in a high-temperature-hot-water tub like ****, and the oil level of 1-butanol is taken out from a high-temperature-hot-water tub after ***** to the marked line, it cools, and mass (m_4) is measured correctly.

[0061]It fills with the distilled water from which the gas which boils a specific gravity bottle and is dissolving was removed, and dips in a high-temperature-hot-water tub like ****, and the oil level of distilled water is taken out from a high-temperature-hot-water tub after ***** to the marked line, it cools, and mass (m_5) is measured correctly.

[0062]Size D_{311} of the microcrystal of the existence of nickel₃Sn₄ and/or nickel₃Sn₂ and the [311] directions of a nickel₃Sn₄ phase was measured to the negative electrode active material of the samples 1-3. This measuring method is shown below.

[0063]The existence of nickel₃Sn₄ and/or nickel₃Sn₂ was first measured with the <size [of the microcrystal of the existence of nickel₃Sn₄ and/or nickel₃Sn₂, and the [311] directions of a nickel₃Sn₄ phase] D_{311} > X-ray diffraction method. The measuring condition is as follows.

[0064]X ray light source: CuK alpha rays (monochrome-ized by the graphite monochromator)
 X-ray output: -- 40 kV - 100-mA divergent slit: -- 1 / 2deg distraction slit: -- 1 / 2deg light-receiving slit: -- 0.15-mm measurement angle : 25 degree<= 2θ <=40 degree [0065]Here, the X diffraction pattern of the metallic material produced with the sample 1 is shown in drawing 2. From drawing 2, it has checked that nickel₃Sn₄ and/or nickel₃Sn₂ were compounded. It was checked that FeSn₂ is compounded by the metallic material of the sample 2, and it was checked that nickel₃Sn₄ and/or nickel₃Sn₂ do not exist in the negative electrode active material of the sample 3.

[0066]Next, when a nickel₃Sn₄ phase existed, it asked for D_{311} by the formula of Scherrer. About the test cell of the sample 1 produced as mentioned above - the sample 3, in order to carry out characterization of a cell, the charge and discharge test was done, and the charging capacity, service capacity, and coulomb efficiency of the cell were searched for. The method of characterization is shown below.

[0067]<the characterization of a cell> -- first, to each test cell, a current value is made into 0.2 mA/cm², constant current charge is performed, if the voltage 0.0V (Li⁺/Li) between terminals is reached, a current value will be extracted, and charge was terminated when the current value reached below 0.01mA/[cm]². The value which broke by negative-electrode-active-material weight quantity of electricity used when carrying out this charge was made into charging capacity (unit: mAh/g).

[0068]Next, a current value is made into 0.2 mA/cm², constant current discharge is performed, and discharge was terminated when cell voltage fell to 1.5V (Li⁺/Li). The value which broke by negative-electrode-active-material weight quantity of electricity used when carrying out this discharge was made into service capacity (unit: mAh/g).

[0069]Coulomb efficiency was calculated from the service capacity and charging capacity which were produced by **** by making it like. Here, coulomb efficiency is a value obtained because Li applies 100 to the value which shows within a cell whether it was used effectively, and broke service capacity by charging capacity.

[0070]The result of size D_{311} of the microcrystal of the [311] directions of the true density produced by making it above and a nickel₃Sn₄ phase, a unit weight, the charging capacity of the cell per unit volume and service capacity, and coulomb efficiency is shown in Table 1.

[0071]

[Table 1]

| | 真密度 (g/cm^3) | D_{311} (nm) | 充電容量 (mAh/g) | 放電容量 (mAh/g) | 充電容量 (mAh/cm^3) | 放電容量 (mAh/cm^3) | クーロン効率 (%) |
|-------|-----------------------------------|-------------------|-----------------------------------|-----------------------------------|--------------------------------------|--------------------------------------|---------------|
| サンプル1 | 8.3 | 16.4 | 574 | 440 | 4764 | 3652 | 76.7 |
| サンプル2 | 7.8 | — | 360 | 280 | 2808 | 2184 | 77.8 |
| サンプル3 | 2.1 | — | 345 | 300 | 725 | 630 | 86.9 |

[0072]It turned out that the nonaqueous electrolyte secondary battery of the sample 1 using the negative electrode active material which contains the metallic material which consists of Li, Sn and Li which are the elements to alloy, and nickel which is the elements which are hard to alloy from Table 1 is a cell which has high capacity since the service capacity per unit volume is dramatically high.

[0073]On the other hand, the cell of the sample 3 which uses the carbon material as negative electrode active material was understood that the service capacity per unit volume is

dramatically small, and cell capacity is low. The cell of the sample 2 using Fe as Li and an element which is hard to alloy had the small service capacity per unit weight as compared with Li and the cell of the sample 1 using nickel as an element which is hard to alloy, and it turned out that coulomb efficiency is inferior.

[0074]Therefore, by using the negative electrode active material containing the metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy as a nonaqueous electrolyte secondary battery showed having very high capacity and becoming a thing provided with the high performance which is not in the former.

[0075]Next, the metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy, And the cell using this metallic material as negative electrode active material was produced, and the battery characteristic was evaluated to the difference of size D_{311} of the microcrystal of a difference of the true density of a metallic material, and the [311] directions of a $\text{nickel}_3\text{Sn}_4$ phase.

[0076]When producing sample 4 metallic material, the test cell was produced like the sample 1 except performing ball mill operation for 60 hours.

[0077]When producing sample 5 metallic material, the test cell was produced like the sample 1 except performing ball mill operation for 120 hours.

[0078]When producing sample 6 metallic material, the test cell was produced like the sample 1 except performing ball mill operation for 250 hours.

[0079]The test cell was produced like the sample 1 except using the metallic material which put the powder mixture 5g into the agate mortar, and was fully mixed with the pestle as sample 7 negative electrode active material.

[0080]True density was measured about the metallic material of the samples 4-7 produced as mentioned above. The measuring method is the same as the measuring method mentioned above.

[0081]Size D_{311} of the microcrystal of the existence of $\text{nickel}_3\text{Sn}_4$ and/or $\text{nickel}_3\text{Sn}_2$ and the [311] directions of a $\text{nickel}_3\text{Sn}_4$ phase was measured to the metallic material of the samples 4-7. This measuring method is the same as the measuring method mentioned above. Thereby, it was checked by the metallic material of the sample 4 - the sample 6 that $\text{nickel}_3\text{Sn}_4$ and/or $\text{nickel}_3\text{Sn}_2$ are compounded. It was checked by the metallic material of the sample 7 that $\text{nickel}_3\text{Sn}_4$ and/or $\text{nickel}_3\text{Sn}_2$ are not compounded.

[0082]About the test cell of the sample 4 produced as mentioned above - the sample 7, in order to carry out characterization of a cell, the charge and discharge test was done, and the charging capacity, service capacity, and coulomb efficiency of the cell were searched for. The

method of characterization is the same as the method of characterization mentioned above.
 [0083]The result of size D_{311} of the microcrystal of the [311] directions of the true density of the metallic material produced by making it above and a nickel₃Sn₄ phase, a unit weight, the charging capacity of the cell per unit volume and service capacity, and coulomb efficiency is shown in Table 2.

[0084]

[Table 2]

| | 真密度 (g/cm ³) | D_{311} (nm) | 充電容量 (mAh/g) | 放電容量 (mAh/g) | 充電容量 (mAh/cm ³) | 放電容量 (mAh/cm ³) | クーロン効率 (%) |
|-------|-----------------------------|-------------------|-----------------|-----------------|--------------------------------|--------------------------------|---------------|
| サンプル4 | 7.5 | 18.4 | 545 | 404 | 4087 | 3030 | 74.1 |
| サンプル5 | 6.8 | 18.4 | 578 | 420 | 3930 | 2856 | 72.3 |
| サンプル6 | 6.4 | 21.0 | 510 | 320 | 3264 | 2048 | 62.7 |
| サンプル7 | 7.5 | — | 750 | 260 | 5625 | 1950 | 34.7 |

[0085]From Table 2, if the cell of the sample 4 and the sample 7 is compared, the cell of the sample 4 which contains nickel₃Sn₄ and/or nickel₃Sn₂ in a metallic material, It turned out that service capacity is high in a metallic material, and coulomb efficiency is better for it than the cell of the sample 7 which does not contain nickel₃Sn₄ and/or nickel₃Sn₂. Therefore, a nonaqueous electrolyte secondary battery has higher capacity, and by containing nickel₃Sn₄ in a metallic material showed that it was highly efficient.

[0086]When the cell of the sample 5 and the sample 6 was compared, the cell of the sample 5 whose true density of a metallic material is 6.8g/cm³ was understood that coulomb efficiency is good rather than the cell of the sample 6 whose true density of a metallic material is 6.4g/cm³. Therefore, as for the true density of the metallic material, it was preferred that it is more than 6.5 g/cm³, and, thereby, it turned out that a nonaqueous electrolyte secondary battery has higher capacity.

[0087]The sample 4 to which the size of the microcrystal of the [311] directions contains the nickel₃Sn₄ phase which is 20 nm or less from Table 2 if the cell of the sample 4 and the sample 6 is compared, [311] The containing-nickel₃Sn₄ phase with larger size of microcrystal of direction than 20 nm sample 6 showed excelling in service capacity. Therefore, as for the metallic material, it was preferred to contain the nickel₃Sn₄ phase whose size of the microcrystal of the [311] directions is 20 nm or less, and it turned out that it becomes what has higher capacity as a nonaqueous electrolyte secondary battery by this.

[0088]

[Effect of the Invention]Since negative electrode active material contains the metallic material which consists of nickel which is Li, Sn and Li which are the elements to alloy, and an element which is hard to alloy at least, the nonaqueous electrolyte secondary battery built over this invention so that clearly also from the above explanation has very high capacity, and turns into a rechargeable battery which is high performance rather than before.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a sectional view of the nonaqueous electrolyte secondary battery which applied this invention.

[Drawing 2]It is a figure showing the X diffraction pattern of the metallic material produced with the sample 1.

[Description of Notations]

1 A nonaqueous electrolyte secondary battery and 2 [A positive electrode can, six separators, 7 insulating gaskets] A negative electrode and 3 A negative electrode can and 4 An anode and 5

[Translation done.]

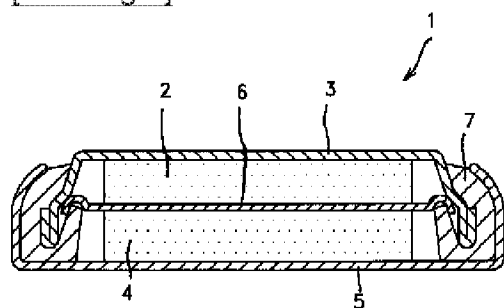
* NOTICES *

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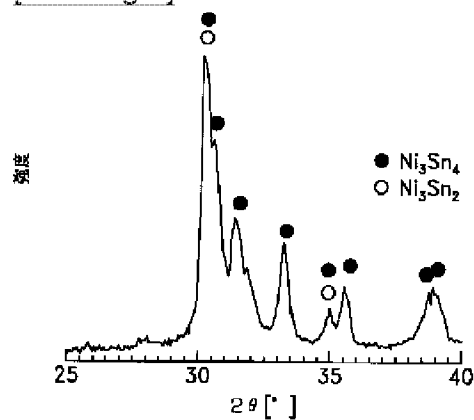
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]